REMOVAL OF HEXAVALENT CHROMIUM FROM CONTAMINATED WATER BY USING A NOVEL ADSORBENT; CERIUM BASED POLYANILINE.

A Dissertation

Submitted in partial fulfilment for the degree of

MASTER OF SCIENCE IN CHEMISTRY

By

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UNDER THE SUPERVISION
Of
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DECLARATION

The work embodied in this report is an original investigation carried out by the author, on the topic entitled, "Removal of Hexavalent Chromium from Contaminated Water by Using a Novel Adsorbent; Cerium Based Polyaniline", for partial fulfilment of degree in Master of Science (Chemistry), NIT Rourkela. To the best of my knowledge and belief, this work has not been submitted to any other University or Institution to confer any Degree or Diploma.

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CERTIFICATE

This is to certify that the project report entitled, "*Removal of Hexavalent Chromium from Contaminated Water by Using a Novel Adsorbent; Cerium Based Polyaniline*", is being submitted to National Institute of Technology, Rourkela by Mr. Manas Ranjan Pradhan, Roll number 409CY2021 for partial fulfilment of the Master of Science degree, Chemistry, which is an original work carried out under my guidance and supervision. This work has not been submitted by him for any other degree to any other Institution or University.

The present study is a valuable contribution for the advancement of knowledge in the field of material chemistry and its environmental application.

In habit and character Mr. Manas Ranjan Pradhan is quite a fit and proper person for the further research work.

I wish him all success in his future life.

Prof. R.K. PATEL
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ABSTRACT

In this work extensive study has been carried out to understand the removal efficiency of chromium (VI) by a hybrid material, cerium based Polyaniline. Among the various techniques, adsorption is one of the most suitable methods which can be adopted to remove hazardous ions from water and waste water. The development of low cost adsorbent is essential for the benefit of the common people. The hybrid material cerium based polyaniline has been synthesized and characterized by XRD, SEM and AAS. Experiments were conducted in batch mode to know the removal efficiency of chromium (VI) by this material as a function of pH, adsorbent dose, temperature, initial concentration and time. The removal efficiency of the hybrid material was 91 % at pH-7, adsorbent dose of 0.08 g/10ml, contact time 50 minutes and temperature 50°C from the aqueous solution having initial Cr (VI) concentration of 10 mg/L. From this study it is infer that this material is having high potential to remove chromium (VI) and other toxic metal which require further study.

Keywords: Hybrid material, ion-exchange, XRD, SEM, AAS.

1. INTRODUCTION

1.1. Chromium Chemistry

The two primary forms of chromium are trivalent chromium, Cr (III), and hexavalent chromium Cr (VI). Trivalent chromium is required by plants and animals in low doses and hexavalent chromium is an environmental pollutant. All compounds of chromium are coloured, the most important compounds are the chromates of sodium and potassium and the dichromates. Lead chromate is chrome yellow, a valued pigment. Chromium is a lustrous, brittle, hard metal. Its colour is silver-grey. It does not tarnish in air, when heated it burns and forms the green chromic oxide. Cr (III) ions are rarely present at pH values over 5, because hydrated chromium oxide [Cr $(OH)_3$] is hardly water soluble. This element exists in nature mainly in two oxidation states, +3 and +6. The melting point of chromium is 1907°C. The relation between Cr (III) and Cr (VI) strongly depends on pH and oxidative properties of the location, but in most cases, the Cr (III) is the dominating species. Chromium (III) ions tend to form octahedral complexes. The colours of these complexes are determined by the ligands attached to the Cr centre. The commercially available chromium (III) chloride hydrate is the dark green complex $[CrCl_2(H_2O)_4]Cl$. Closely related compounds have different colours: pale green $[CrCl(H_2O)_5]Cl_2$ and the violet $[Cr(H_2O)_6]Cl_3$. If water-free green chromium (III) chloride is dissolved in water then the green solution turns violet after some time, due to the substitution of water by chloride in the inner coordination sphere. This kind of reaction is also observed with solutions of chrome alum and other water-soluble chromium (III) salts. Chromium (III) hydroxide (Cr $(OH)_3$) is amphoteric, dissolving in acidic solutions to form $[Cr(H_2O)_6]^{3+}$, and in basic solutions to form $[Cr(OH)_6]^{3-}$. It is dehydrated by heating to form the green chromium (III) oxide (Cr_2O_3), which is the stable oxide. Cr (VI) is powerful oxidants at low or neutral pH. Most important are chromate anions (CrO_2^{-4}) and dichromate ($Cr_2O_7^{2-}$) anions, which exist in equilibrium:

$$2\ [CrO_4]^{2-} + 2\ H^+ \rightleftarrows [Cr_2O_7]^{2-} + 2\ H_2O$$

Chromium (VI) halides are known also and include hexafluoride CrF_6 and chromyl chloride (CrO_2Cl_2). Sodium chromate is produced industrially by the oxidative roasting of chromite ore with calcium or sodium carbonate. The dominant species is therefore, by the law of mass action, determined by the pH of the solution. The change in equilibrium is visible by a change from yellow (chromate) to orange (dichromate), such as when an acid is added to a neutral solution of potassium chromate. At yet lower pH values, further condensation to more complex oxyanions of chromium is possible.

Both the chromate and dichromate anions are strong oxidizing reagents at low pH.

$$Cr_2O_7^{2-} + 14\ H_3O^+ + 6\ e^- \rightarrow 2\ Cr^{3+} + 21\ H_2O$$

They are, however, only moderately oxidizing at high pH.

$$CrO_4^{2-} + 4\ H_2O + 3\ e^- \rightarrow Cr(OH)_3 + 5\ OH^-$$

1.2. Sources of chromium

Chromium does not occur freely in nature. The main chromium mineral is chromite ($FeOCr_2O_3$). As it was mentioned earlier, chromium compounds can be found in waters only in trace amounts. The element and its compounds can be discharged in surface water through various industries. It is applied for example for metal surface refinery and in alloys. Stainless steel consists of 12-15% chromium. Chromium metal is applied worldwide in amounts of approximately 20,000 tons per year. It may be polished and it does not oxidize when it comes in contact with air. The metal industry mainly discharged trivalent chromium. Hexavalent chromium in industrial waste waters mainly originates from tanning and painting. Chromium compounds are applied as pigments, and 90% of the leather is tanned by means of chromium compounds. Waste water usually contains about 5 ppm of chromium. Chromium may be applied as a catalyser, in wood impregnation, in audio and video production and in lasers. Chromite is the starting product for inflammable material and chemical production.

Chromium may be present in domestic waste from various synthetic materials. Through waste incineration it may spread to the environment when protection is insufficient.

1.3. Chromium Applications

Chromium (IV) oxide (CrO_2) is used to manufacture magnetic tape. Chromium is used to give glass an emerald green colour. Chromium compounds are used in the textile industry as mordrants, and by the aircraft and other industries for anodizing aluminium. The refractory industry has found chromite useful for forming bricks and shapes, as it has a high melting point, moderate thermal expansion, and stability of crystalline structure. Chromium is used as in fabrication of alloys, in preparation of alloy steels to enhance corrosion and heat resistance, in fabrication of plated products for decoration or increased wear resistance, in production of non-ferrous alloys to impart special qualities to the alloys, in production and processing of insoluble salts, as chemical intermediates, in textile industry in dyeing, silk treating, printing, and moth proofing wool, in leather industry in tanning and in photographic fixing baths, as catalysts for halogenations, alkylation, and catalytic cracking of hydrocarbons, as fuel additives and propellant additives in ceramics. The main functions of Chromium in the body is Regulation of blood , Moderates cholesterol levels, Contributes to lean muscle mass, Promotes arterial health, Boosts immune system, Stimulates protein synthesis.

1.4. Chemistry of Chromium Toxicity

Since Cr (III) is poorly absorbed by any route of the human body, the toxicity of chromium is mainly attributable to the Cr (VI) form. It can be absorbed by the lung and gastrointestinal tract, and even to a certain extent by intact skin. The reduction of Cr (VI) is considered to serve as a detoxification process when it occurs at a distance from the target site for toxic or genotoxic effect while reduction of Cr (VI) may serve to activate chromium toxicity if it takes place in or near the cell nucleus of target organs. If Cr (VI) is reduced to Cr (III) extracellular, this form of the metal is not readily transported into cells and so toxicity is

not observed. The balance that exists between extracellular Cr (VI) and intracellular Cr (III) is what ultimately dictates the amounts and rates at which Cr (VI) can enter cells and impart its toxic effects. Cr (VI) enters many types of cells and under physiological conditions can be reduced by hydrogen peroxide (H_2O_2), glutathione (GSH) reductase, ascorbic acid, and GSH to produce reactive intermediates, including Cr (V), Cr (IV), thiyl radicals, hydroxyl radicals, and ultimately, Cr (III). Any of these species could attack DNA, proteins, and membrane lipids, thereby disrupting cellular integrity and functions.

1.5. Environmental effects of chromium

Trivalent chromium is required for plants. Chromium (VI) compounds are toxic at low concentrations for both plants and animals. Hexavalent chromium is very toxic to flora and fauna. Chromium (III) oxides are only slightly water soluble; therefore concentrations in natural waters are limited. Chromium (VI) compounds are stable under aerobic conditions, but are reduced to Cr (III) compounds under anaerobic conditions. The reverse process is another possibility in an oxidizing environment. Chromium at concentrations of between 500 and 6000 ppm in soils, are not dangerous for plants. Lime or phosphate in soils may further decrease chromium susceptibility. Under normal conditions plants contain approximately 0.02-1 ppm chromium (dry mass), although values may increase to 14 ppm. In mosses and lichens, relatively high chromium concentrations can be found. The mechanism of chromium toxicity is pH dependent. Soluble chromates are converted to insoluble chromium (III) salts and consequently, availability of chromium for plants decreases. This mechanism protects the food chain from high amounts of chromium. Chromate mobility in soils depends on both soil pH and soil sorption capacity, and on temperature. The guideline for chromium is agricultural soils is approximately 100 ppm. Seawater chromium content varies strongly, and is usually between 0.2 to 0.6 ppb. Rivers contain approximately 1 ppb of chromium. Phytoplankton contains approximately 4 ppm chromium, sea fish contain 0.03 to 2 ppm, and oyster tissue contains approximately 0.7 ppm (all values dry mass). In dissolved form

chromium is present as either anionic trivalent Cr $(OH)_3$ or as hexavalent [CrO_4^{2-}]. The amount of dissolved Cr (III) ions is relatively low, because the Cr (III) complexes are stable. Chromium (III) compounds are water insoluble because these are largely bound to floating particles in water. Chromium (III) oxide and chromium (III) hydroxide are the only water soluble compounds. Chromium (VI) oxide is an example of an excellently water soluble chromium compounds, solubility = 1680 g/L. As chromium compounds were used in dyes and paints and the tanning of leather, these compounds are often found in soil and groundwater at abandoned industrial sites, now needing environmental clean-up and remediation for the treatment of brown field land. Primer paint containing hexavalent chromium is still widely used for aerospace and automobile refinishing applications. Chromium enters the air, water and soil in the chromium (III) and chromium (VI) form through natural processes and human activities. Crops contain systems that arrange the chromium-uptake to be low enough not to cause any harm. But when the amount of chromium in the soil rises, this can still lead to higher concentrations in crops. Chromium is not known to accumulate in the bodies of fish, but high concentrations of chromium, due to the disposal of metal products in surface waters, can damage the gills of fish that swim near the point of disposal.

1.6. Chromium related health hazards

Water insoluble Cr (III) compounds and chromium metal are not considered a health hazard, while the toxicity and carcinogenic properties of Cr (VI) have been known for a long time. Because of the specific transport mechanisms and bigger size, only limited amounts of Cr (III) enter into the cells. Several in vitro studies indicated that high concentrations of Cr (III) in the cell can lead to DNA damage. The human body contains approximately 0.03 ppm of chromium. Daily intake strongly depends upon feed levels, and is usually approximately 15-200 μg, but may be as high as 1 mg. The placenta is the organ with the highest chromium amounts. Cr (III) is an essential trace element for humans. Chromium deficits may enhance

diabetes symptoms. Chromium can also be found in RNA. Cr (III) toxicity is unlikely, at least when it is taken up through food and drinking water. It may even improve health, and cure neuropathy and encephalopathy. Cr (VI) is known for its negative health and environmental impact, and its extreme toxicity. It causes allergic and asthmatic reactions, is carcinogenic and is 1000 times as toxic as Cr (III). Health effects related to Cr (VI) exposure include diarrhoea, stomach and intestinal bleedings, cramps, paralysis and liver and kidney damage. Toxic effects may be passed on to children through the placenta. Cr (VI) oxide is a strong oxidant. Upon dissolution chromium acid is formed, which corrodes the organs. People can be exposed to chromium through breathing, eating or drinking and through skin contact with chromium or chromium compounds. The level of chromium in air and water is generally low. In drinking water the level of chromium is usually low as well, but contaminated well water may contain the dangerous Cr (IV), Cr (VI). For most people eating food that contains Cr (III) is the main route of chromium uptake, as Cr (III) occurs naturally in many vegetables, fruits, meats, yeasts and grains. Various ways of food preparation and storage may alter the chromium contents of food. When food is stores in steel tanks or cans chromium concentrations may rise. Cr (III) is an essential nutrient for humans and shortage may cause heart conditions, disruptions of metabolisms and diabetes. But the uptake of too much Cr (III) can cause health effects as well, for instance skin rashes. Cr (VI) is a danger to human health, mainly for people who work in the steel and textile industry. People who smoke tobacco also have a higher chance of exposure to chromium. Cr (VI) is known to cause various health effects. The various health effects of Cr (VI) are Respiratory effects, Skin effects, Carcinogenic effects, Renal effects, Hepatic effects, Haematological Effects, Genotoxic and Mutagenic Effects.

Respiratory Effects

Human occupational experience clearly indicates that when inhaled to chromium compounds caused respiratory tract irritants, resulting in airway irritation, airway

obstruction, and lung, nasal, or sinus cancer. Dose exposure duration and the specific compound involved can determine chromium's adverse health effects. The chromium dust can cause pulmonary irritant effects following inhalation. Some of the common respiratory effects are Asthma, Chronic bronchitis, chronic irritation, chronic pharyngitis, chronic rhinitis, congestion and hyperemia, polyps of the upper respiratory tract, tracheobronchitis, and ulceration of the nasal mucosa with possible septal perforation. Many cases of nasal mucosa injury (inflamed mucosa, ulcerated septum, and perforated septum) have been reported in workers exposed to Cr (VI) in chrome-plating plants and tanneries chrome-plating plants.

Skin Effects

Adverse effects of the Cr (VI) form on the skin may include ulcerations, dermatitis, and allergic skin reactions. Some of the skin effects are dryness, erythema, fissuring, papules, scaling, small vesicles, and swelling. Penetration of the skin will cause painless erosive ulceration ("chrome holes") with delayed healing. These commonly occur on the fingers, knuckles, and forearms.

Renal Effects

Although glomerular injury has been noted in chromium workers, the predominant renal injury is tubular, with low doses acting specifically on the proximal convoluted tubules. Injury to the brush border membrane is a feature of chromate nephropathy. Severe poisoning can lead to acute tubular necrosis and acute renal failure. Low-dose chronic Cr (VI) exposure typically results only in transient renal effects.

Hepatic Effects

The reported liver effects include derangement of the liver cells, necrosis, lymphocytic and histolytic infiltration, and increases in Kupffer cells. Cases of hepatic effects after oral exposure to Cr (VI) compounds have also been reported.

Haematological Effects

Cases of haematological effects have been reported in humans after the ingestion of lethal or sub lethal doses of Cr (VI) compounds. In a case of an 18-year-old woman who ingested a few grams of potassium dichromate, decreased haemoglobin content and hematocrit, and increased total white blood cell counts, reticulocyte counts, and plasma haemoglobin were found 4 days after ingestion. These effects were indicative of intravascular homolysis.

Genotoxic and Mutagenic Effects

In one experiment, Cr (VI) plus glutathione induced DNA damage in vitro, whereas Cr (III) with or without glutathione did not. Chromium seems to exert its genetic effects by binding directly to DNA. It can produce stable DNA-chromium complexes, DNA strand breaks, DNA-DNA cross links, and DNA-protein cross links. The active species for DNA binding seems to be the trivalent form Cr (VI) compounds are clearly mutagenic in the majority of experimental situations .It has caused chromosome aberrations in mammalian cells and has been associated with increased frequencies of chromosome aberrations in lymphocytes from chromate production workers.

1.7. Literature review

Chromium toxicity refers to the toxic effects of chromium. Water insoluble chromium (III) compounds and chromium metal are not considered a health hazard, while the toxicity and carcinogenic properties of chromium (VI) have been known for a long time. Because of the specific transport mechanisms, only limited amounts of chromium (III) enter the cells. Several in vitro studies indicated that high concentrations of chromium (III) in the cell can lead to DNA damage. Acute oral toxicity ranges between 1900 and 3300 µg/kg. The proposed beneficial effects of chromium (III) and the use as dietary supplements yielded

some controversial results, but recent reviews suggest that moderate uptake of chromium (III) through dietary supplements poses no risk. World Health Organization recommended maximum allowable concentration in drinking water for chromium (VI) is 0.05 mg/l. Hexavalent chromium is also one of the substances whose use is restricted by the European Restriction of Hazardous Substances Directive. The LD50 for chromium (VI) ranges between 50 and 150 mg/kg. In the body, chromium (VI) is reduced by several mechanisms to chromium (III) already in the blood before it enters the cells. The chromium (III) is excreted from the body, whereas the chromate ion is transferred into the cell by a transport mechanism, by which also sulfate and phosphate ions enter the cell. The acute toxicity of chromium (VI) is due to its strong oxidation properties. After it reaches the blood stream, it damages the kidneys, the liver and blood cells through oxidation reactions. Hemolysis, renal and liver failure are the results of these damages. Aggressive dialysis can improve the situation. The carcinogenity of chromate dust is known for a long time, and in 1890 the first publication described the elevated cancer risk of workers in a chromate dye company. Three mechanisms have been proposed to describe the genotoxicity of chromium (VI). The first mechanism includes highly reactive hydroxyl radicals and other reactive radicals which are by-products of the reduction of chromium (VI) to chromium (III). The second process includes the direct binding of chromium (V), produced by reduction in the cell, and chromium (IV) compounds to the DNA. The last mechanism attributed the genotoxicity to the binding to the DNA of the end product of the chromium (III) reduction. Chromium salts (chromates) are also the cause of allergic reactions in some people. Chromates are often used to manufacture, amongst other things, leather products, paints, cement, mortar and anti-corrosives. Contact with products containing chromates can lead to allergic contact dermatitis and irritant dermatitis, resulting in ulceration of the skin, sometimes referred to as "chrome ulcers". This condition is often found in workers that have been exposed to strong chromate solutions in electroplating, tanning and chrome-producing manufacturers.

1.7.1. Treatment options

(a) Coagulation/filtration removes chromium by co precipitation and adsorption using iron coagulants. Coagulation/filtration using alum is already used by some utilities to remove suspended solids and may be adjusted to remove chromium.

(b) Iron oxide adsorption filters the water through a granular medium containing ferric oxide. Ferric oxide has a high affinity for adsorbing dissolved metals such as chromium. The iron oxide medium eventually becomes saturated, and must be replaced.

(c) Ion Exchange has long been used as a water-softening process, although usually on a single-home basis. It can also be effective in removing chromium with a net ionic charge.

(d) Both Reverse osmosis and electro dialysis (also called electrodialysis reversal) can remove chromium with a net ionic charge. Some utilities presently use one of these methods to reduce total dissolved solids and therefore improve taste.

1.8. Aims and Objective

Keeping the above factors in view the present research work has been undertaken with the following objectives.

(a) To synthesis and characterize the Cerium based Polyaniline.

(b) To utilize the material to know the removal efficiency of Cr (VI).

(c) To find the optimum condition for removal of Cr (VI).

(d) To formulate a process for field application.

(e) To know the structure and removal mechanisms.

2. EXPERIMENTAL SECTION

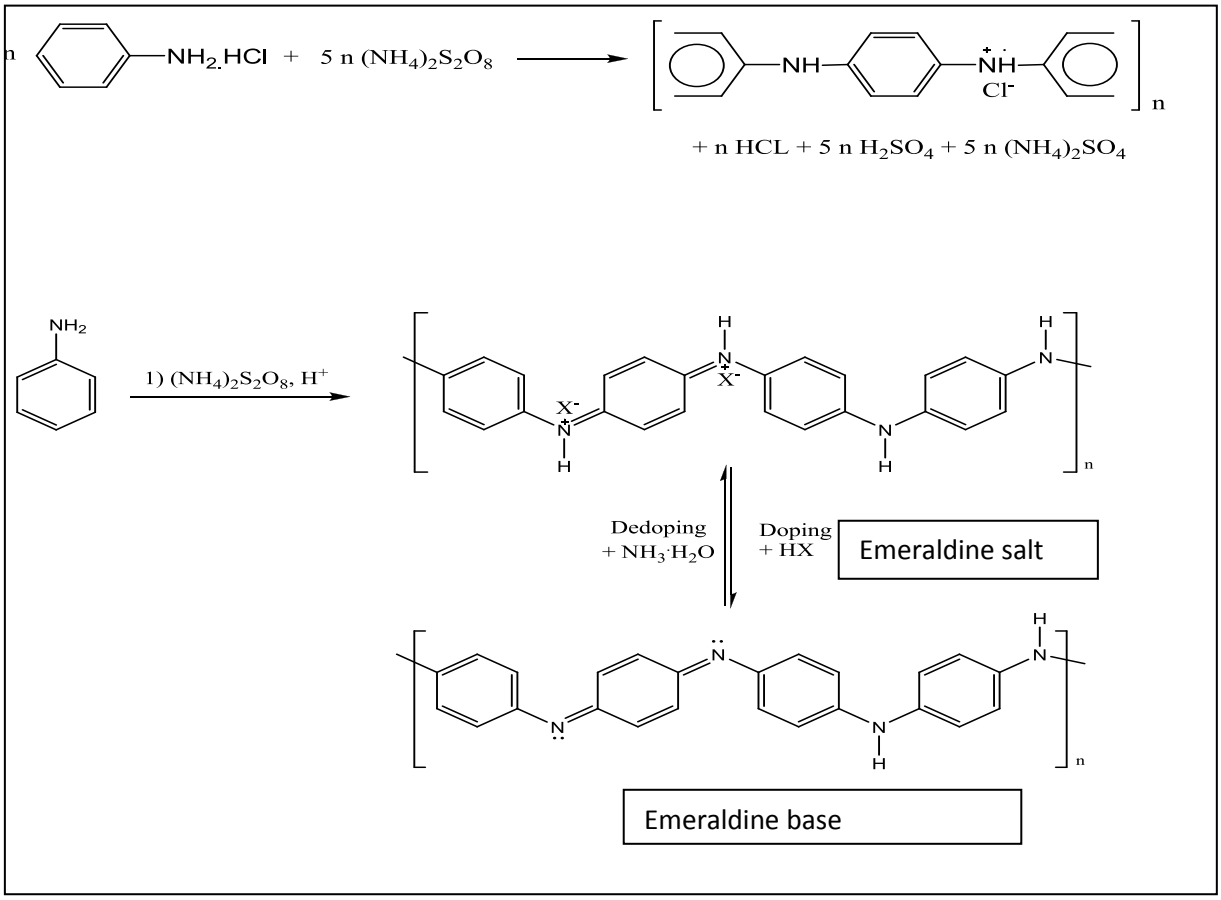
2.1. Materials and Methods

All chemicals used for this study was of AR grade. All glassware like measuring cylinder, volumetric flask, conical flask, etc., were of borosil and tarson make .Cerium nitrate [Ce $(NO_3)_3.6H_2O$] and aniline [C_6H_7N] were used for the synthesis of the hybrid material. Standard solution of chromium (VI) was prepared from potassium dichromate ($K_2Cr_2O_7$). HCl and Ammonium hydroxide (NH_4OH) were used to maintain the pH. The other instruments used in this study are pH meter (elico), AAS (Perkin Elmer PE Analyst Atomic Absorption Spectroscopy), XRD (Phillips Powder Diffract meter Model PW 1830), SEM (JEOL, jXA-8100).

2.2. Synthesis of Polyaninline and Cerium based Polyaniline

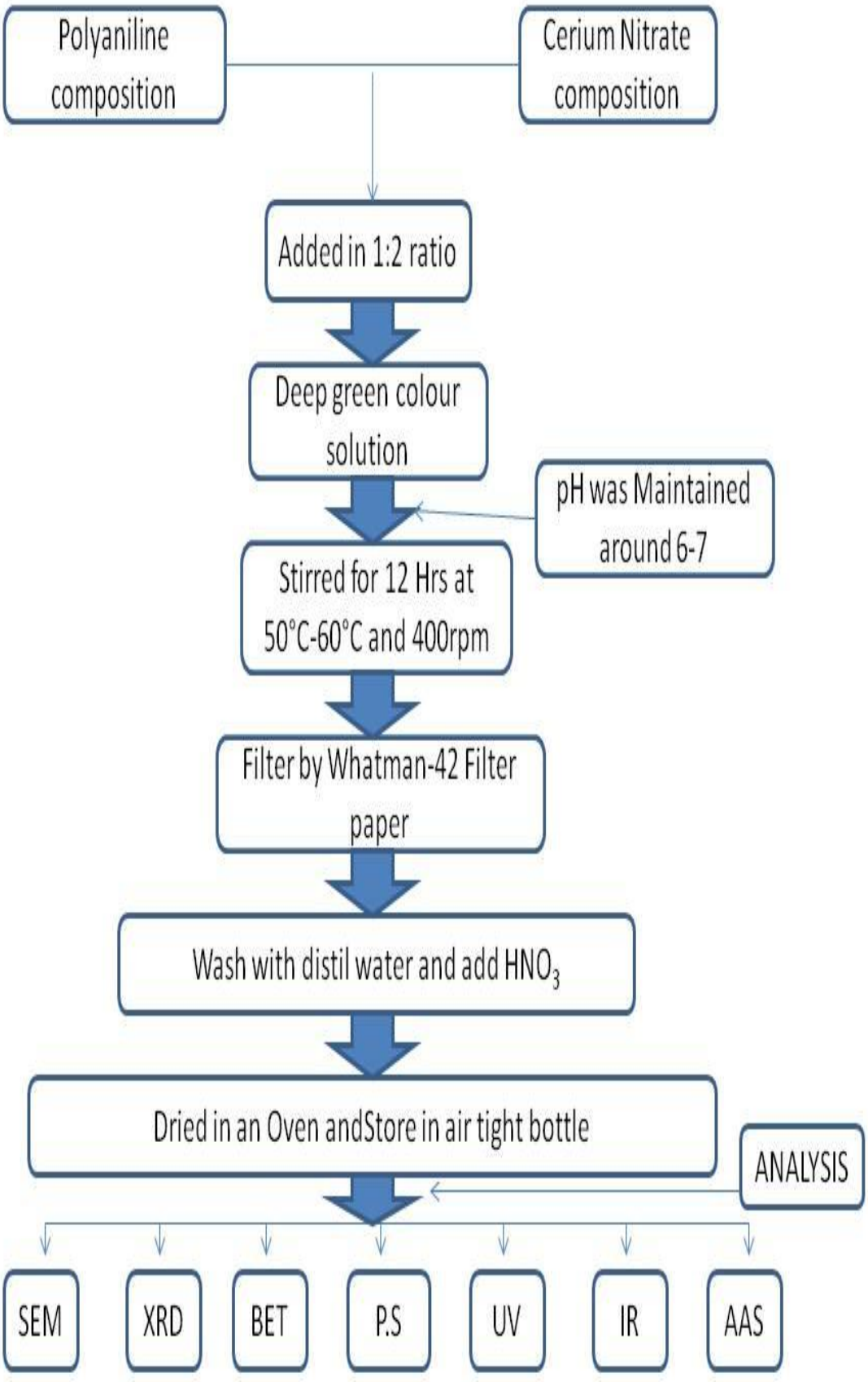
20 ml (0.219M) aniline was dissolved in 300ml (1M) aq. HCl, 11.5 gm (0.050M) of ammonium perdisulfate [$(NH_4)_2S_2O_8$] was dissolved in 200ml of 1M HCl and 500ml (0.1M) ammonium hydroxide. Polyaniline ppt. was obtained by mixing the above two solutions at a very low temperature i.e. 0-4° C (using ice bath) and stirred for 1.5 Hours. It was then filtered and washed with HCl and ammonium hydroxide. Then the ppt. was dried in an oven at 50°-60°C for overnight and fine powder of polyaniline was obtained. 100 ml of cerium nitrate (0.1M) solution was taken in a burette and 0.2gm of Polyaniline power was taken in a 100ml beaker. Then the cerium nitrate solution was added drop wise to the polyaniline powder. Then the pH was maintained around 6-7 by using conc. NH_4OH and conc. HCl. The reaction was carried out for 12 hours on a magnetic stirrer at 60°C and 400rpm. Then add 2-3 drops of HNO_3 for acid activation. Then the solution was filtered and the material was washed with double distilled water. Then the material was dried in an oven at 50°C and stored in an air tight bottle for further study. The chromium concentration was measured by AAS (Perkin Elmer PE Analyst Atomic Absorption Spectroscopy).The X-ray diffraction (XRD) analysis were done over a range of 10° to 90° using Phillips Powder Diffractometer Model PW 1830 at

a scan speed of 2°/min. The surface morphology of the hybrid material were studied using scanning electron microscope (JEOL, jXA-8100).



Structure of the Polyaninline before cerium induced.

2.3. Flow chart for synthesis of Cerium Based Polyaniline



3. RESULT AND DISCUSSION

3.1. Characterization of Cerium Based Polyaniline

The present study is under taken to synthesis and characterize of Cerium Based Polyaniline and its application for the removal of Cr (VI) from synthetic solution. The material is characterized based on the data of analysis of SEM, TGDTA, XRD, FTIR, UV-VIS, CHNS, NMR and the report of the similar work. The chemical analysis and elemental analysis of the material is presented in (Table 1.) the material forms a polymeric matrix, In order to identify the chemical stability, the material was kept in 20 mL of different mineral acids, bases and salt solutions of different concentration for 12Hr and the supernatant liquid was examined for cerium (Table 2). The material reveals high chemical stability, and was found that the material was quite stable in most of the mineral acids and salt solutions. The main physicochemical parameters of the contaminated water are listed in (Table 3).

Table- 1: Chemical analysis and elemental analysis of present hybrid material

	N%	*C%*	*H%*	*S%*
Ce-Polyaninline Hybrid material	1.002145	59.85412	4.213545	4.08796

Element	App Conc.	Weight%	Atomic%
C K	183.14	60.73	76.79
N K	0.26	1.10	1.19
O K	26.11	21.15	20.07
Cl K	0.61	0.30	0.13
Ce L	33.82	16.73	1.81

Table-2: chemical stability of the hybrid material

Solvent (50 mL)	Stability
1M H_2SO_4	Partially Dissolved
2M H_2SO_4	Partially Dissolved
4M H_2SO_4	Partially Dissolved
1M HNO_3	Insoluble
2M HNO_3	Insoluble
4M HNO_3	Insoluble
1M HCL	Insoluble
2M HCL	Insoluble
4M HCL	Insoluble
1M NaOH	Partially soluble
2M NaOH	Partially soluble
4M NaOH	Partially soluble
1M NH_4OH	Insoluble
2M NH_4OH	Insoluble
4M NH_4OH	Insoluble

Table- 3: physicochemical parameters of the contaminated water

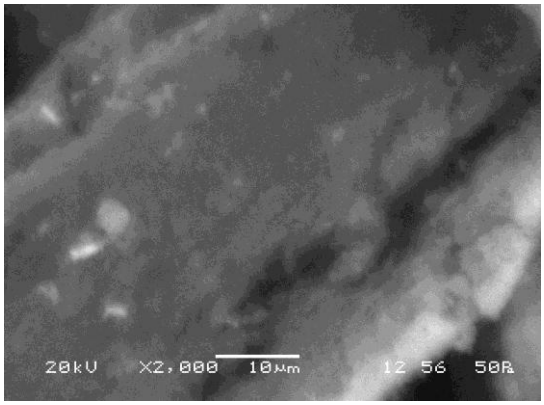
Mg^{2+}	60.32 mg/L
Ca^{2+}	129.66 mg/L
TH(Total Hardness)	177.20 mg/L
COD	13.66 mg/L
TOC	0.2 mg/L
Cl^-	57.46 mg/L
Fe^{3+}	0.16 mg/L
SO_4^{2-}	61.28 mg/L
NO_3^{2-}	4.52 mg/L
F	0.002 mg/L
Hg^{2+}	NIL mg/L
Cd^{2+}	0.001 mg/L
Cr (VI)	0.003 mg/L
Al^{3+}	0.001 mg/L
Pb^{2+}	0.001 mg/L
As^{3+}	0.003 mg/L
Cu^{2+}	0.02 mg/L

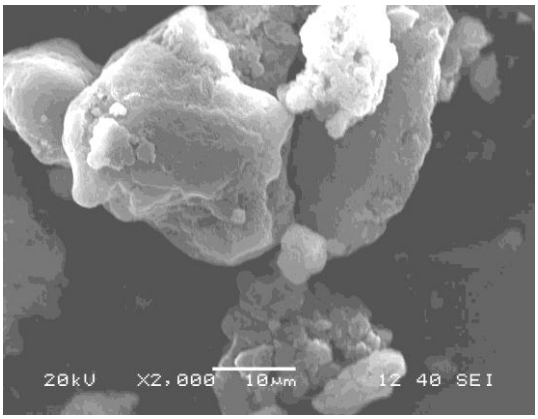
3.1.1. SEM micrographs of Cerium based Polyaniline material

The surface morphology of the material is studied by Scanning electron microscopy (SEM) is presented in (Figure 1). The SEM image before adsorption and after adsorption clearly indicates the change in the surface morphology. Figure 1a represents before adsorption which indicate that the material do not have identifiable pores. Figure 1b represents after adsorption which clearly indicates the adsorption of Chromium ions on the surface and confirmed by the EDAX.

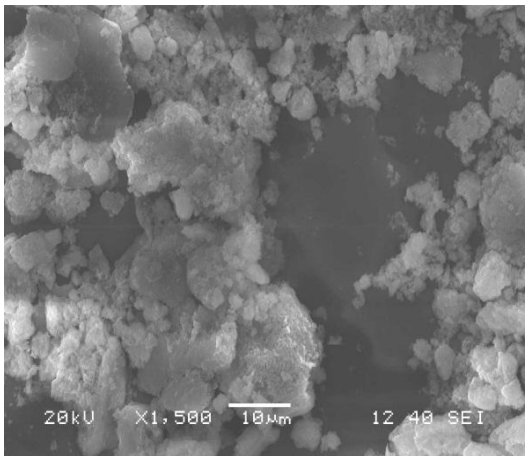
Figure1: SEM Micrographs

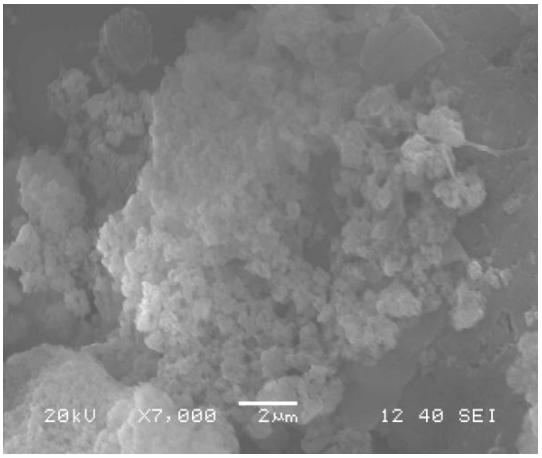
(a) Before Adsorption





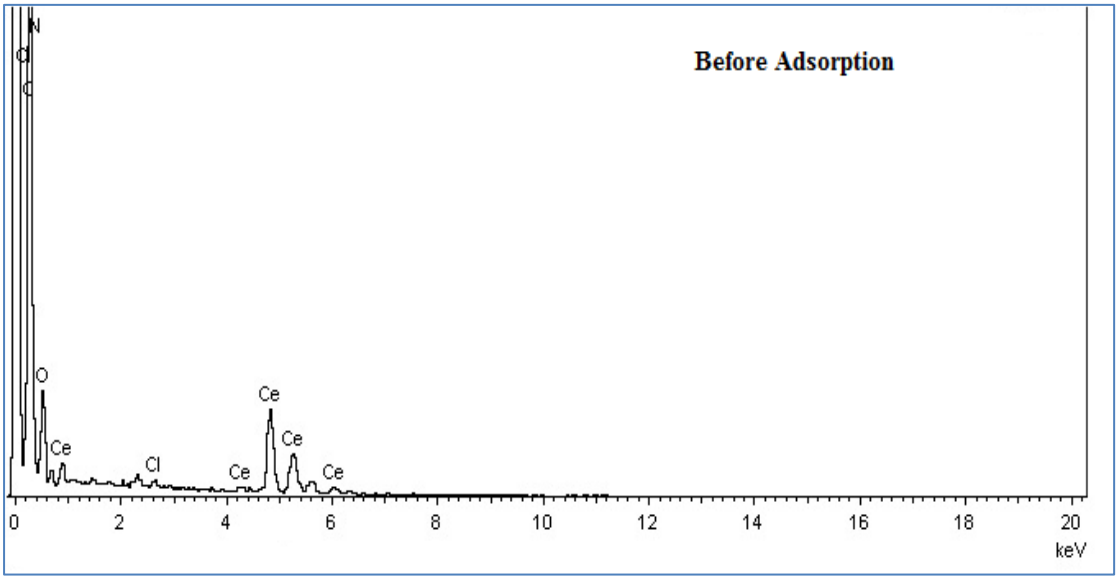
(b) After adsorption

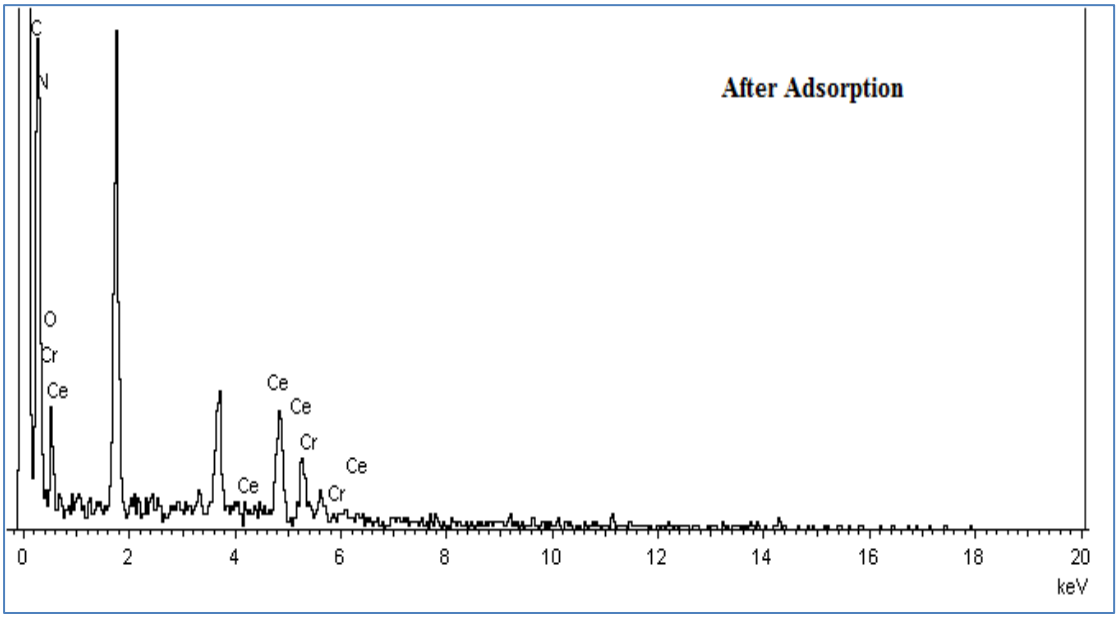




3.1.2. EDAX Study

The EDAX study of the composite material was carried out (Before and after) and got the following figures.





3.1.3. BET study

BET surface area of the material is done through nitrogen adsorption technique and it is found that the material is having a high surface area (Table 4), the specific surface area of the material is not incorporated because the results of the analysis are awaited.

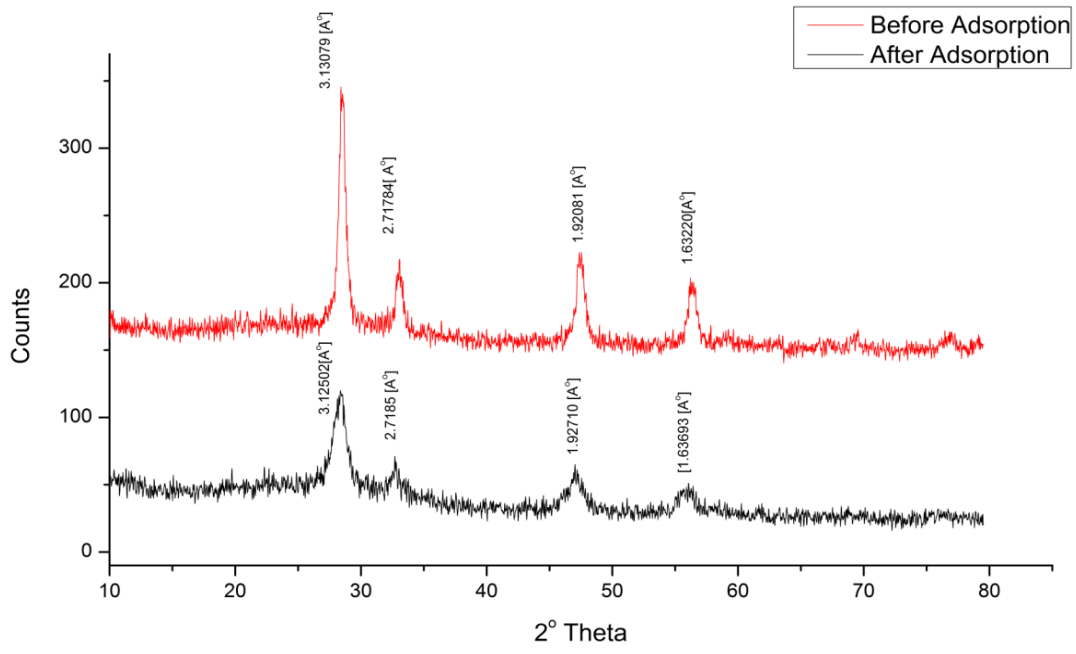
Table-4: BET-Isotherm report of the hybrid material

Property	Method	Ce-Polyaninline Hybrid Material
Specific surface area (m^2/g)	Nitrogen adsorption	
Pore Volume (Cm^3/g)	Nitrogen adsorption	
pore diameter	Nitrogen adsorption	

3.1.4. XRD study

The XRD pattern of the sample is presented in (Figure. 2); Sharp peaks were obtained indicating the sample was crystalline. XRD pattern was analysed using standard software. A few intense peak of cerium polyaniline with a d-spacing of 3.13079 [A^O] at, 2 theta 28.50 ^{o} is found and volume of the cell is 160.20, before adsorption which is supported by the JCPDES file number 64-0507.

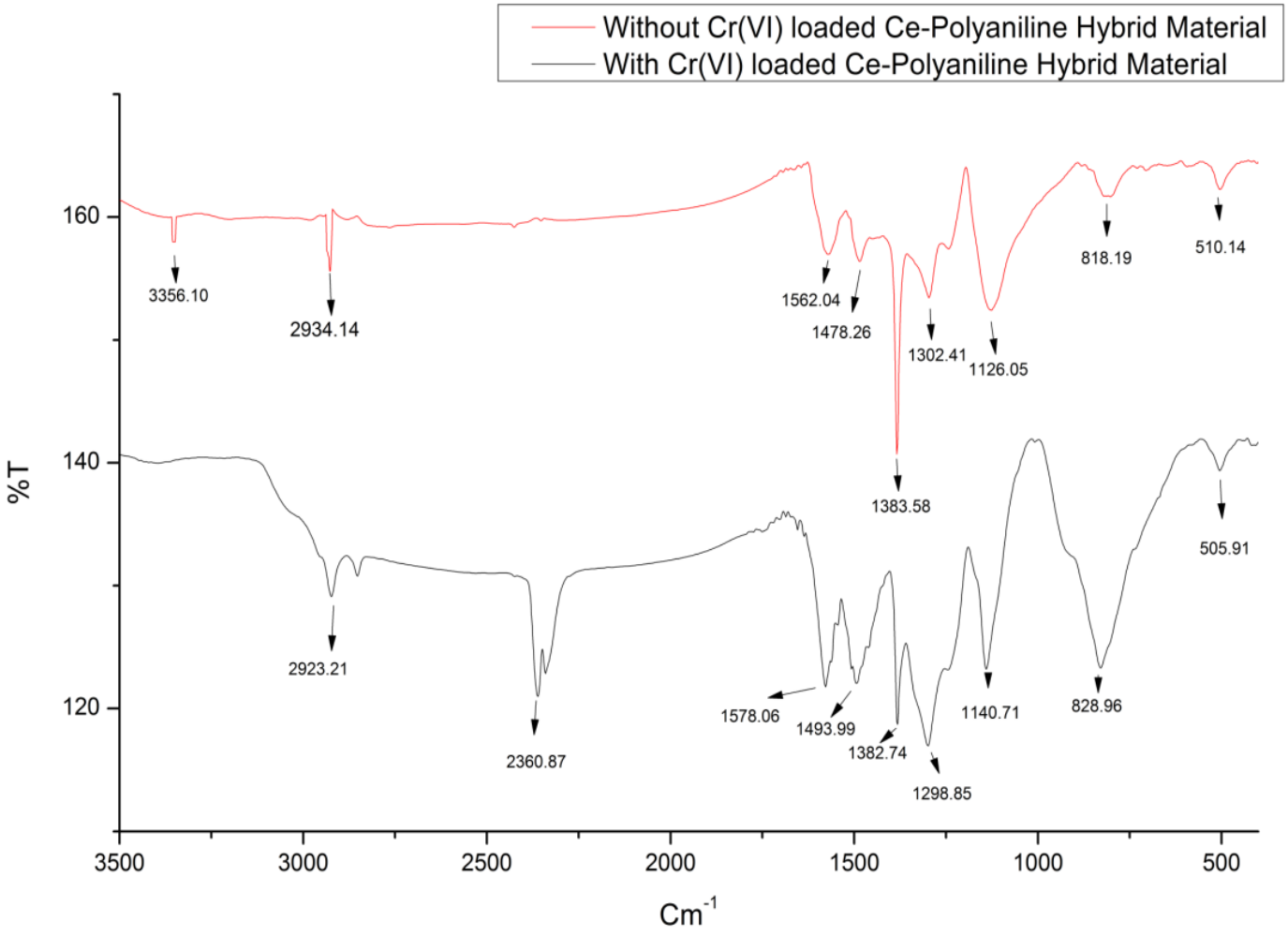
Figure 2: XRD plot of Cerium based polyaniline



3.1.5. FTIR study

FTIR study of the sample was carried out (Figure. 3) in order to know the presence of different groups and structures in the material. The presence of band at 3356.10 cm^{-1} is due to bonded OH groups, NH stretching, which indicates the presence of water of crystallization. Further, the presence of a peak at 2934.14 cm^{-1} in cerium based polyaniline hybrid material is due to the presence of NH bending. This peak is found to be shifted with slight broadening after adsorption at 2923.21 cm^{-1}, which is an indication of bonding of the dichromate anion ($Cr_2O_7^{2-}$). The peak at 818.19 cm $^{-1}$ and 510.15 cm $^{-1}$ in cerium polyaniline is assigned to metal- oxygen bonding is further shifted after adsorption towards 828.96 cm-1 and 505.91 cm^{-1}. The peaks at 1126.05 cm^{-1} and 1140.71 cm^{-1} are due to C-C stretching. The peaks at 1478.26 cm^{-1} and 1493.99 cm^{-1} are due to C=C stretching.

Figure 3: FTIR Study of the Hybrid material before adsorption and after adsorption



3.1.6. Particle size analysis.

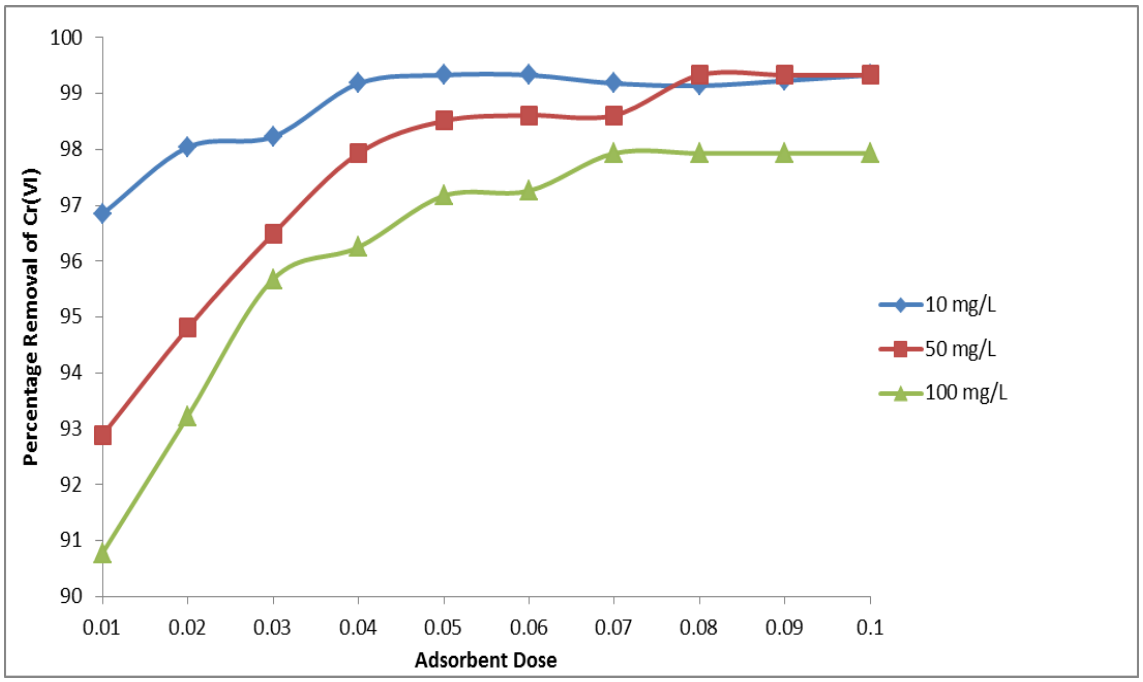
From the particle size analysis the particle size of the hybrid material was found to be 1032 nm.

3.2. Batch Study of the hybrid material

3.2.1. Effect of Adsorbent Dose

The effect of adsorbent dose on the removal of hexavalent chromium is investigated in neutral condition (pH 7), at ambient temperature (27±2 ^{o}C) and contact time of 30 minute for initial hexavalent chromium concentration of 10mg/L, 50mg/L and 100mg/L. The results are presented in (Figure 5). It is evident from the (Figure 5) that the removal of hexavalent chromium increases from 96.85 to 99.33 %, 92.89 to 99.33% and 90.78% to 97.93% for 0.01 – 0.1 g/10ml of cerium polyaniline hybrid material respectively with initial chromium (VI) concentration of 10mg/L, 50mg/L and 100mg/L. It is observed that after dosage of 0.08g/10 ml, there is no significant change in percentage of removal of hexavalent chromium. It may be due to the overlapping of active sites at higher dosage. So, 0.08g/10ml is considered the optimum dose and is used for further study.

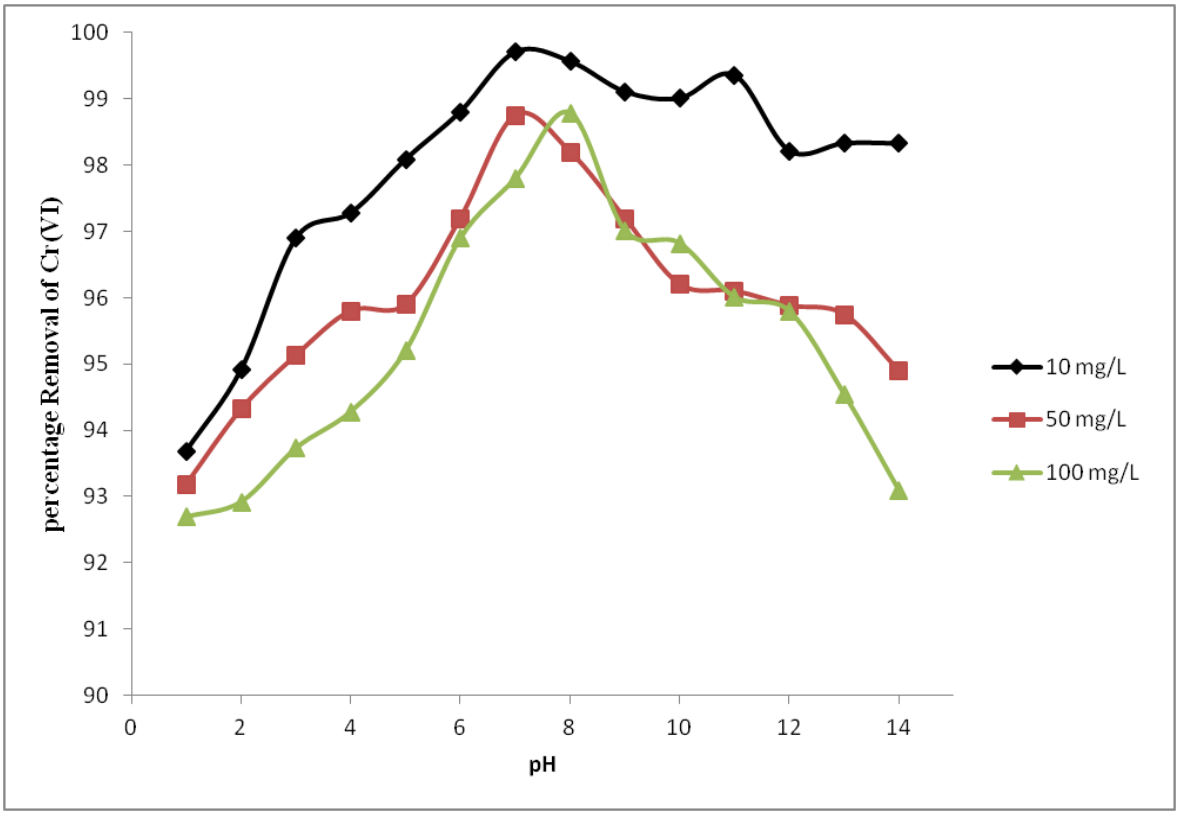
Figure 5: Effect of adsorbent dose on the removal percentage of chromium (VI) removal



3.2.2. Effect of pH

Percentage removal of hexavalent chromium at different pH is studied in batch experiments using 0.08 g of adsorbent in 10 mL aqueous solution, at ambient temperature (27±2 ^{o}C), contact time of 30 minute for initial hexavalent chromium concentration of 10mg/L, 50mg/L, and 100mg/L. The results are presented in (Figure 6). The pH of the solution after adsorption is measured and is found to increase or decrease slightly without any regular trend. It is evident from the graph that there is removability at pH 2 and to pH 8 almost 93.1 % removal and the highest removal was achieved at pH higher than 5 but below 8. This decrease of chromium (VI) uptake at alkaline pH could be due to competition for active sites by excessive amount of hydroxyl ions.

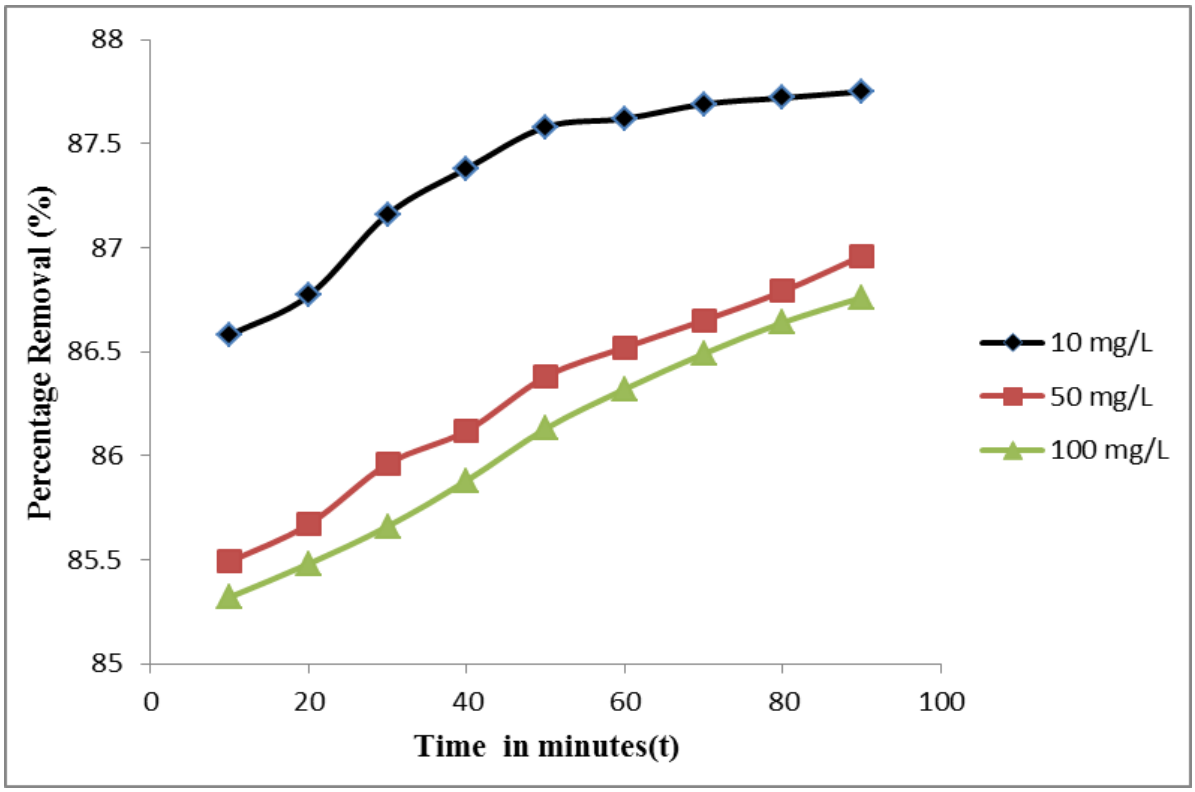
Figure 6: Effect of pH on the removal of Chromium (VI) from the contaminated water



3.2.3. Effect of contact times

Batch study of chromium (VI) at different contact time is studied for initial chromium (VI) concentration of 10mg/L, 50mg/L and 100mg/L at pH 7 and adsorbent dose of 0.08 g/10 ml keeping all other parameters constant. The result is represented in (Figure 7). It is clear from the (Figure 7) that more than 86 % removal takes place within 50 min and equilibrium is reached after 50 min. The transformation in the rate of removal might be due to the fact that initially all adsorbent sites are unoccupied and also the solute concentration gradient is high. Later the chromium (VI) uptake rate by adsorbent is decreased suggestively, due to the decrease in the number of adsorption sites as well as hexavalent concentration.

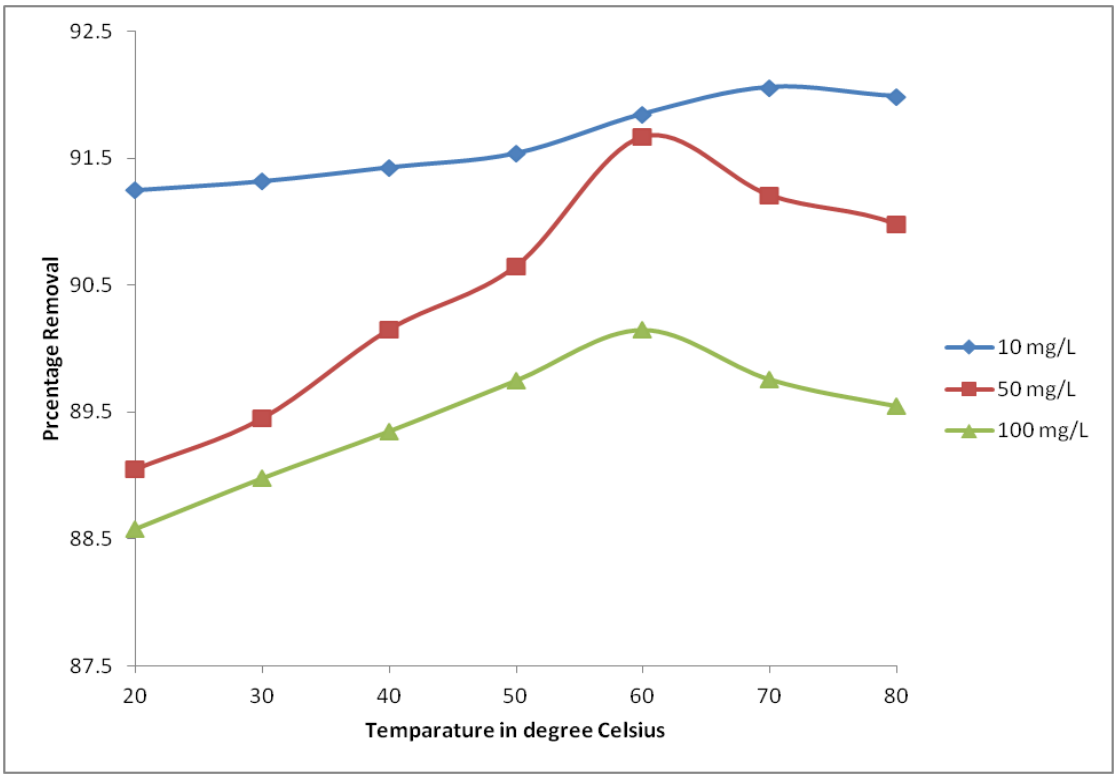
Figure 7: percentage removal of Cr (VI) from the CE-Polyaniline based material versus Contact time



3.2.4. Effect of Temperature

The consequence of temperature on the adsorption of chromium (VI) with initial concentration 10mg/L, 50 mg/L and 100 mg/L is studied using optimum adsorbent dose (0.08 g/10mL) and at contact time of 50 minutes. The results are represented as percentage removal of hexavalent chromium) versus temperature (Figure 8). The percentage removal of hexavalent chromium with initial concentration 10mg/L, increased from 91.25 % to 91.99 %, for 50 mg/L, increased from 89.05 % to 99.04 % and for 100 mg/L, increased from 88.58 % to 89.38% for 25 to 45° C temperatures respectively. From the (Figure 8) that, at the temperature between 50^{o} Celsius to 60 ^{o} Celsius the removal was almost 91 % and with increase in temperature the percentage removal decrease slowly and reached almost 88 %.

Figure 11: Effect of temperature on the removal of Cr (VI) from the CE-polyaniline based material

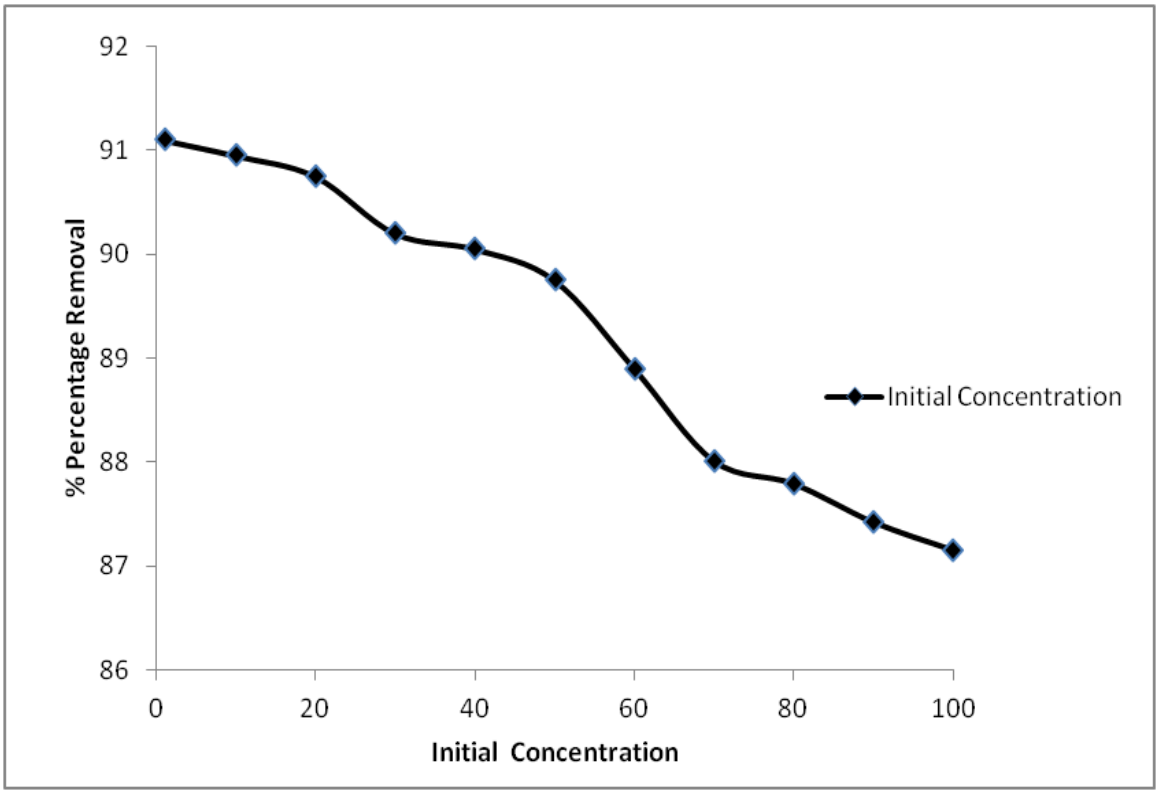


3.2.5. Effect of initial Hexavalent chromium concentration

The adsorption of hexavalent chromium onto hybrid material is calculated by varying initial hexavalent chromium concentration using optimum adsorbent dose (0.08g/10ml) at ambient temperature (27±2 ^{o}C) and contact time of 50 min. The results are signified in graphical form as percentage removal versus initial hexavalent chromium concentration in (Figure 8). The initial hexavalent chromium concentration is increased from 10mg/L to 100 mg/L and the corresponding removal gradually decreases from 91 % to 87 %. It is observed from the (Figure 8) that, there is a decrease in removal percentage with increase in initial hexavalent chromium concentration due to the fact that at greater adsorbate concentration, the free sites available approaches overload.

Figure 8: percentage removal of Cr (VI) from the CE-polyaniline based material

Versus initial Hexavalent Chromium concentration



4. Conclusion

From the above studies the following conclusion are drawn which helps for further studies. The hybrid material is crystalline in nature as evident from XRD data. From SEM-EDAX report it is confirmed that the hybrid material is membrane in nature the specific surface area of the material is not incorporated because the results of the analysis are awaited. The Cr (VI) removal efficiency of the synthetic material are conducted by varying parameters like contact time, pH, amount of adsorbent, and temperature to know the optimum conditions. The hybrid material was found to have a maximum removal efficiency of 91 % at pH-7, adsorbent dose of 0.08 g/10ml, contact time 50 minutes and temperature 50°C from 10mg/L of the chromium (VI) synthetic solution. From all the results it may be concluded that the material is appropriate to act as an adsorbent for the removal of Cr (VI) from contaminated water and which require further study.

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